

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C09D 11/00, 11/10	A1	(11) International Publication Number: WO 99/07796 (43) International Publication Date: 18 February 1999 (18.02.99)
(21) International Application Number: PCT/GB97/02106 (22) International Filing Date: 5 August 1997 (05.08.97) (71) Applicant (for all designated States except US): SERICOL LIMITED [GB/GB]; Burnash Castrol House, Pipers Way, Swindon, Wiltshire SN3 1RE (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): SMITH, Brian [GB/GB]; 8 Mountbatten Way, Brabourne Lees, Ashford, Kent TN25 6PZ (GB). (74) Agent: LEWIS, Pauline, T.; Burmah Castrol Trading Limited, Group Patents Dept., Burmah Castrol House, Pipers Way Swindon, Wiltshire SN3 1RE (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: AN INK JET INK (57) Abstract <p><u>A water-based, flash-curable ink jet ink that is capable of adhering to plastic substrates such as flexible polyvinyl chloride, the ink comprising: a) at least one water-dispersible or water-soluble acrylate polymerisable material; b) at least one polymerisable material that is capable of softening the substrate in part or in full and is resistant to hydrolysis; c) at least one colourant such as a pigment, a dye or both a pigment and a dye; and d) at least one UV photoinitiator.</u></p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

An Ink Jet Ink

The present invention concerns an ink jet ink, and in particular a water-based, flash-curable ink jet ink that is capable of adhering to difficult substrates such as matt or gloss uncoated vinyl surfaces.

Printed ink jet inks on substrates are currently cured by medium and high pressure mercury vapour UV lamps. One of the disadvantages of using these lamps is that they are switched on for long periods of time which causes a high degree of heat to be produced and makes it necessary to have sophisticated cooling equipment. The cooling equipment produces either a high air flow or water cooling. The cooling equipment is bulky and it is expensive to incorporate it into an ink jet printing machine. Failure to cool the UV lamp causes distortion of the substrate. The other disadvantages of using a standard UV lamp are: surfaces exposed to the UV lamp need to be equidistant from the lamp in order to achieve uniform curing; and the UV lamp can cause yellowing of the cured surface.

WO 94/11123 has overcome the disadvantages of a standard UV-curable lamp by proposing the use of a high energy electronic flash source and the use of photoinitiators that correspond to the radiation emitted from the flash source. WO 94/11123 discloses a flash curable protective coating that is printed on to optical articles made of plastic (see Example 6). The protective coating comprises 30-40 parts multifunctional melamine acrylate; 70-60 parts trifunctional reactive thinner; 0.5-1.5 parts p-phenyl benzophenone; 1.5-3 parts methyl methyl thiophenyl morpholinopropane; and 0.1-0.5 parts polyether modified dimethyl polysiloxane copolymers.

The inventor of the present invention coated flexible polyvinyl chloride with the protective coating disclosed in Example 6 of WO 94/11123 and found that the coating cracked badly when the polyvinyl chloride was folded through 180°. The

protective coating disclosed in WO 94/11123 is therefore not suitable for printing on to difficult plastic substrates such as flexible polyvinyl chloride.

The present invention is concerned with the problem of providing a water-based, flash-curable ink jet ink that is capable of adhering to difficult plastic substrates such as flexible polyvinyl chloride laminates that are used in display signs.

In accordance with the present invention there is provided a water-based, flash-curable ink that is capable of adhering to difficult plastic substrates such as flexible polyvinyl chloride, the ink comprising:

- a) at least one water dispersible or water soluble acrylate polymerisable material;
- b) at least one polymerisable material that is capable of softening the substrate in part or in full and is resistant to hydrolysis;
- c) a colourant such as a pigment, a dye or both a pigment and a dye; and
- d) at least one UV photoinitiator.

The present inventors have found that the ink defined above is capable of adhering to difficult plastic substrates such as flexible polyvinyl chloride.

By the term 'polymerisable material' we intend to include monomers, prepolymers and oligomers.

The water dispersible or water soluble acrylate polymerisable material is preferably a water dispersible or water soluble urethane acrylate oligomer.

The polymerisable material in part b) is preferably a monomer, and the monomer is preferably 1,6-hexane diol diacrylate (HDDA). HDDA is a difunctional acrylate that offers a high cure rate. HDDA also exhibits excellent compatibility with and solvency for other oligomers and additives used in the ink.

The water dispersible or water soluble acrylate polymerisable material may be non-ionic or anionic. The water dispersible or water soluble acrylate polymerisable

material preferably has a molecular weight between 400 and 1,500, more preferably between 700 and 1,100, as measured by size exclusion chromatography. The non-volatile content of the polymerisable material may be between 10 and 100%.

The photoinitiator may comprise one or more photoinitiators and also a synergist. The photoinitiator preferably has a quantum yield in the range 0.1 to 1.0. The photoinitiator should not function as a chain transfer agent or terminating agent.

The preferred photoinitiators are Lucerin TPO acyl phosphine oxide (sold by BASF), Irgacure 369 (sold by Ciba-Geigy) and Darocure 1173 (sold by Ciba-Geigy). Darocure 1173 is a useful solvent for the Lucerin TPO and the Irgacure 369. The Lucerin TPO and Irgacure 369 are preferably used in amounts ranging from 0.1 to 1.0%, based on oligomer solids. The Irgacure is preferably used in an amount ranging from 0.1 to 3.0%, based on oligomer solids. 4-benzoyl biphenyl is also a useful photoinitiator.

The pigment may be dispersed in the ink using any one of the known methods that produces a fine particle size of less than 1 micron. The pigment may also be added to the ink in a dispersed form.

Examples of suitable pigments are: Yellow 13 and 83; Red 9, 184 and 188; Blue 15:3; Green 7; and Black 7. The reader is directed to US-A-5,160,372 for further examples of suitable pigments.

The dye may be selected from known dyes that are used in ink jet systems. The reader is directed to US-A-5,160,372 for examples of suitable dyes.

The ink can include any of the usual additives that are present such as: surfactants, UV stabilisers, waxes and rheology modifiers.

The present invention will now be described by way of the following Examples:

Examples

Test to Find a Polymerisable Material that is capable of Softening a Plastic Substrate such as Polyvinyl Chloride and is Resistant to Hydrolysis

In order to test whether any of the selection of monomers listed below are capable of softening a plastic substrate such as polyvinyl chloride, a small drop of each of the monomers was placed on to a polyvinyl chloride substrate. After being left for 5 minutes, the monomers were removed from the polyvinyl chloride using a soft cloth and the surface of the polyvinyl chloride was examined for softening and marking. The results are as follows:

Monomer	Result
Tripropyleneglycol diacrylate	no mark
Ethoxylated trimethylol propane triacrylate	no mark
Trimethyl propane triacrylate	no mark
2 phenoxyethyl acrylate	no mark
Di-propylene glycol diacrylate	no mark
N vinyl caprolactam*	substrate softened
N N di-vinyl imidazole*	substrate softened
N vinyl pyrrolidone	substrate softened
Hexane diol diacrylate	substrate softened
N vinyl formamide	substrate softened
Neopentyl glycol diacrylate	no mark
Octyldecyl acrylate	substrate softened
Iso bornyl acrylate	no mark
Lauryl acrylate	no mark

* 50% solutions in TPGDA since they are solid at ambient temperature.

The results show that only six out of the fifteen monomers that were tested were capable of softening the polyvinyl chloride surface.

Test For Monomer's Hydrolysis Resistance:

In order for the monomer to be used in a water-based ink, it needs to be resistant to hydrolysis. The five monomers that were capable of softening the polyvinyl chloride were tested for their resistance to hydrolysis. The monomers were tested for their hydrolytic stability under both acidic and basic conditions. Ten percent dispersions of the monomers were prepared in deionised water, with the pH being adjusted to 5 and 9 with dilute HCl and NaOH respectively. The samples were stored for 1 week at 40 °C and then checked for degradation using HPLC. Of the monomers tested, hexane diol diacrylate (HDDA) gave the best resistance properties.

Test for Monomer's Compatibility with other Components in the Ink:

The monomer's compatibility with other components in the ink was tested by formulating the ink and checking for general problems such as separation on storage. The test was carried out using HDDA and the HDDA was found to be compatible with the ink's other components.

Test to Find a Water-Dispersible or Water-Soluble Acrylate
Polymerisable Material

Test for Solubility:

In the inks of the present invention the water-dispersible or water-soluble acrylate polymerisable material is preferably soluble in the polymerisable material that softens the substrate, so that it imparts stability to the polymer dispersion. We tested whether a selection of acrylate oligomers were soluble in HDDA by preparing 25% solids solutions of a range of oligomer types in HDDA and the solutions were examined for clarity and stability towards separation. The solubility is largely linked to molecular weight within a group of similar oligomers: the lower molecular weight examples have the best solubility. High molecular weight examples, however,

impart good flexibility so a combination of both high and low molecular weight examples is used to give optimum performance.

The test revealed that acrylate and methacrylate copolymers are the preferred oligomers.

Hydrolytic Stability:

The acrylate oligomers were not tested for their hydrolytic stability in isolation. No particular problems were encountered with hydrolytic stability of the oligomers used in the previous tests. Methacrylate copolymers were selected on the basis that their other properties were suitable and that they are well known for their hydrolytic stability. Experimental ink samples were however checked for changes in pH on storage. A decrease in pH indicates hydrolysis problems.

Test to Find a Suitable Photoinitiator

In order to maximise on the efficiency of the initiators, it is necessary to match the absorption characteristics of the initiator and the pigment with the output from the energy source. The wavelength and radiant energy of a light source may be measured with a Spectral Radiometer. The absorption of a photoinitiator may be determined using a scanning UV/visible spectrometer.

Test Results

The following photoinitiators were found to be suitable:

	<u>UV Absorption Range</u>
Lucerin TPO acyl phosphine oxide	355 to 410nm
Irgacure 369	280 to 440nm (peaking at 340nm)
Daracure 1173	225 to 275nm (peaking at 245nm)

4 benzoyl biphenyl

225 to 325nm (peaking at 290nm)

Preparation of Inks

The following inks were prepared:

Example 1

		<u>Parts w/w</u>
Part A	Actilane SP061	10
	HDDA	89
	Igepal CA897 (emulsifying agent)	1
	Water	100
Part B	Actilane 640 (water dispersible urethane acrylate)	200
	Lucerin TPO	2
	Pigment dispersion	10
	Fluorad FC129 (surfactant)	0.6
	Methyl diethanolamine (pH adjuster)	1

Example 2

Part A	Actilane SP061	10
	HDDA	89
	Igepal CA897 (emulsifying agent)	1
	Water	100
Part B	Halwedol 14/40w	200
	Lucerin TPO	2
	Pigment dispersion	10

Fluorad FC129 (surfactant)	0.6
Methyl diethanolamine	1

Example 3

Part A	Actilane SP061	10
	HDDA (monomer)	89
	Igepal CA897 (emulsifying agent)	1
	Water	100
Part B	Actilane 640	200
	Lucerin TPO	1.4
	Darocure IM3	8
	Pigment dispersion	8
	Fluorad FC129 (surfactant)	0.6

In the above Examples, best results were obtained using from 40 to 60% by weight of Part A and from 60 to 40% by weight of Part B.

Comparative Example 1

Part A	Actilane SP061	10
	TPGDA	89
	Igepal CA897	1
	Water	100
Part B	Actilane 640	200
	Lucerin TPO	0.8
	Benzophenone	0.5
	Darocure 1173	0.5
	Irgocur	1
	Pigment dispersion	8

Fluorad FC129

0.6

Comparative Example 2

Part A	Actilane SP061	10
	HDDA	89
	Igepal CA897	1
	Water	100
Part B	Actilane 640	100
	Isopropyl thioxanthone	3
	(available as QUANTACURE ITX from International Biosynthetics)	
	Ethyl 4 di-methylanions benzoate	2
	(available as QUANTACURE EPD from International Biosynthetics)	
	Pigment dispersion	8
	Fluorad FC129	0.6

Method of Preparation of Inks

The inks were prepared by the following steps:

- a) the Actilane SP061 was dissolved in the HDDA;
- b) the emulsifying agent was dissolved in the water;
- c) the dissolved Actilane SP061 was added to the dissolved emulsifying agent using a Silverson disperser running at high speed and fitted with an emulsifying head. The emulsion was stirred for approximately 30 minutes;
- d) the water dispersible urethane acrylate was added to the emulsion using the Silverson at slow speed;
- e) the photoinitiator was added to the emulsion and the emulsion was stirred;
- f) the speed of the Silverson disperser was increased and the pigment dispersion was added;

g) the surfactant and pH adjuster were added to the emulsion while the emulsion was being slowly stirred.

It is important to note that the particles in the ink should be less than 5 microns in diameter, and more preferably less than 1 micron. This is because ink jet heads have nozzles that are 50 microns in diameter and large particles in the ink cause blockages.

Test Method

The inks were tested for their adhesion to difficult plastic substrates using the following test method:

The inks were applied to a plastic laminate, such as those sold under the trade names of MACTAC MACSCREEN or INTERCOAT P, to a coat weight of 67 gsm (equivalent to 600 x 600 dpi). After applying the inks to the substrate, the inks were cured using 10 flashes at 600 joules/ flash.

To test for adhesion of the films to the substrate:

- 1) the films were scratched with a finger nail and then they were checked for damage;
- 2) the substrate was folded through 180° and the films were checked for damage at the fold line; and
- 3) Cellotape was placed on to the films and pressed down. It was then ripped from the film and the film was checked for damage.

Test Results

The inks prepared in Examples 1, 2 and 3 exhibited good adhesion to an uncoated gloss polyvinyl chloride surface. The ink prepared in Comparative Example 1

exhibited poor adhesion to an uncoated gloss polyvinyl chloride surface. The ink prepared in Comparative Example 2 did not cure under the conditions of the test.

Claims

1. A water-based, flash-curable ink jet ink that is capable of adhering to plastic substrates such as flexible polyvinyl chloride, the ink comprising:
 - a) at least one water-dispersible or water-soluble acrylate polymerisable material;
 - b) at least one polymerisable material that is capable of softening the substrate in part or in full and is resistant to hydrolysis;
 - c) at least one colourant such as a pigment, a dye or both a pigment and a dye; and
 - d) at least one UV photoinitiator.
2. The water-based, flash-curable ink jet ink as claimed in claim 1, wherein the water dispersible or water soluble acrylate polymerisable material is a water dispersible or water soluble urethane acrylate oligomer.
3. The water-based, flash-curable ink jet ink as claimed in claims 1 or 2, wherein the polymerisable material in part b) is a monomer, and the monomer is preferably hexane diol diacrylate.
4. The water-based, flash-curable ink jet ink as claimed in claim 2, wherein the oligomer is an acrylate or methacrylate copolymer.
5. The water-based, flash-curable ink jet ink as claimed in any one of the preceding claims, wherein at least 25 parts by weight of water dispersible or water soluble acrylate polymerisable material are dissolved in the polymerisable material in part b).
6. The water-based, flash-curable ink jet ink as claimed in any one of the preceding claims, wherein the ink comprises at least 18%, preferably at least 25%, of water, based on the total weight of the ink.

7. The water-based, flash-curable ink jet ink as claimed in any one of the preceding claims, wherein the water-dispersible or water-soluble acrylate polymerisable material is present in the ink in an amount from 5-15% by total weight.

8. A method of preparation of a water-based, flash-curable ink jet ink that is capable of adhering to plastic substrates such as flexible polyvinyl chloride, the method comprising the following steps:

- a) selecting at least one water-dispersible or water-soluble acrylate polymerisable material;
- b) selecting at least one polymerisable material that is capable of softening the substrate in part or in full and is resistant to hydrolysis;
- c) dissolving the water-dispersible or water-soluble acrylate polymerisable material in the polymerisable material in part b);
- d) selecting at least one UV photoinitiator and adding it to the above mixture;
- e) selecting at least one colourant, such as a pigment, a dye or both a pigment and a dye, and adding it to the above mixture.

9. Use of the water-based, flash-curable ink jet ink defined in any one of claims 1-7 as an ink in an ink jet printer for printing on to plastic substrates such as flexible polyvinyl chloride.

10. A method of ink jet printing, wherein the method comprises the step of using the water-based, flash-curable ink jet ink defined in any one of claims 1-7 in an ink jet printer to print on to plastic substrates such as flexible polyvinyl chloride.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 97/02106

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C09D11/00 C09D11/10		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 C09D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 9516 Derwent Publications Ltd., London, GB; Class A97, AN 95-118887 XP002061516 & JP 07 041 712 A (OSAKA SEALING INSATSU KK) , 10 February 1995 see abstract ---	1-3
A	WO 94 11123 A (LACKFABRIK HCH. JORDAN) 26 May 1994 cited in the application see claims 1,10; example 4 ---	1
A	GB 2 256 874 A (SERICOL LTD.) 23 December 1992 see abstract ---	1
-/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">6 April 1998</div>		Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">17/04/1998</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-weight: bold;">Girard, Y</div>

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/02106

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 623 001 A (MURRAY FIGOV) 22 April 1997 see abstract ---	1
A	EP 0 658 607 A (CANON KABUSHIKI KAISHA) 21 June 1995 see abstract -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/02106

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9411123 A	26-05-94	DE 4336748 A EP 0668800 A	16-06-94 30-08-95
GB 2256874 A	23-12-92	NONE	
US 5623001 A	22-04-97	NONE	
EP 658607 A	21-06-95	JP 7224241 A	22-08-95